

10/553788

## PATENT COOPERATION TREATY


## PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY  
(Chapter II of the Patent Cooperation Treaty)

REC'D 07 FEB 2005

WIPO PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 63138A		<b>FOR FURTHER ACTION</b>		See Form PCT/IPEA/416
International application No. PCT/US2004/013975		International filing date (day/month/year) 05.05.2004		Priority date (day/month/year) 12.05.2003
International Patent Classification (IPC) or national classification and IPC C08L23/16, C08J5/18, C08F2/00, C08F210/16				
Applicant DOW GLOBAL TECHNOLOGIES INC				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 11 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 11 sheets, as follows:</p> <p><input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in Item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input checked="" type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input checked="" type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand  15.11.2004		Date of completion of this report  07.02.2005		
Name and mailing address of the International preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer  Kaumann, E  Telephone No. +31 70 340-3640		



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2004/013975

---

**Box No. I Basis of the report**

---

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-40 as originally filed

**Claims, Numbers**

1-25 received on 16.11.2004 with letter of 12.11.2004

**Drawings, Sheets**

1/1 as originally filed

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/US2004/013975

---

**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

---

**1. Statement**

Novelty (N)	Yes: Claims	
	No: Claims	1-25
Inventive step (IS)	Yes: Claims	
	No: Claims	1-25
Industrial applicability (IA)	Yes: Claims	1-25
	No: Claims	

**2. Citations and explanations (Rule 70.7):**

**see separate sheet**

---

**Box No. VII Certain defects in the international application**

---

The following defects in the form or contents of the international application have been noted:

**see separate sheet**

---

**Box No. VIII Certain observations on the international application**

---

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents:

D1 = US 6,248,831  
D2 = JP 2002 302514  
D3 = US 6,194,520  
D4 = EP 0 503 791  
D5 = US 2002/0042472  
D6 = US 6,147,167  
D7 = EP 0 700 769  
D8 = US 6,485,662

Insofar as a reasoned statement with regard to novelty and inventive step appears useful in view of the numerous clarity problems of the claims, outlined below under items VII and VIII, the following objections are raised:

**1. Novelty (Article 33(2) PCT)**

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of **claims 1 - 25** is not new in the sense of Article 33(2) PCT.

Subject-matter of **claim 1** of the present application is a **process** for producing a multimodal ethylene polymer, comprising  
a first a gas phase step in the presence of a supported Ziegler Natta titanium magnesium catalyst, wherein an  $\alpha$ -olefin and ethylene are polymerized in the presence of hydrogen to produce a high molecular weight polymer, the polymer is transferred to a second gas phase reactor wherein in a second step with a lower comonomer/ethylene ratio a polymer blend is produced.

This blend is molten in an extruder in the presence of a small amount of oxygen at a temperature of 220 to 270 °C and crosslinked to a certain amount. Then, the product is passed through one or more screens.

Subject-matter of **claim 5** is a **multimodal polyethylene composition** having  
a density of at least 0,940 g/cm<sup>3</sup>,  
an MFI (5) of 0,2 to 1,5 g/10 min,  
a melt index ratio of (MFI 21/ MFI 5) of 20 to 50,  
a molecular weight distribution of 20 to 40 and  
a bubble stability , and  
a dart impact of at least 300 g,  
the composition comprises ,

- A) a) a high molecular weight fraction, of from 30 to 70 wt-%,  
b) a density of at least 0,860 g/cm<sup>3</sup>,  
c) a melt flow index (21) of from 0,01 to 50 g/10 min  
d) a melt index ratio (MFI 21/ MFI 5) of 6 to 12, and  
B) a) a low molecular weight fraction from 30 - 70 wt-%,  
b) a density of at least 0,900 g/cm<sup>3</sup>,  
c) a melt flow index (2) of 0,5 to 3000 g/10 min,  
d) a melt index ratio (MFI 21/ MFI 5) of 5 to 15,  
e) prepared using an  $\alpha$ -olefin/ethylene ratio lower than that of the other step.

Subject-matter of **product-by-process claim 10** is a polyethylene composition of claim 5  
produced by the process of claim 1.

Subject-matter of **claim 12** is a multimodal polyethylene composition according to claims  
10 and 11, fabricated into a film.

Subject-matter of **claim 14** is a film comprising the multimodal polyethylene composition of  
claims 10 and 11.

Subject-matter of **claim 15** is a multimodal polyethylene film.

Subject-matter of **claim 16** is the multimodal polyethylene film of claim 15, comprising the  
multimodal composition of claim 5.

Subject-matter of **claim 20** is a multimodal polyethylene composition having a NCLS of at  
least 2400, a ratio of flexural modulus to density of at least 1140 kPa.m<sup>3</sup>/kg, and a melt  
index ratio of at least 90.

Subject-matter of **product-by process claim 21** is a multimodal polyethylene composition  
according to claim 20, produced by the process of claim 1.

Subject-matter of **claims 22 to 25** is a fabricated article made of a multimodal composition

according to any of claims 19, 20 and 21.

**D1** discloses a process for producing a polyethylene blend in two fluidized bed gas phase reactors using a titanium/magnesium catalyst. In the first reactor, a mixture of  $\alpha$ -olefin to ethylene of 0,005 to 0,4 and hydrogen in a ratio of 0,001 to 0,3 mol % to ethylene is polymerized. In the second reactor, a mixture of  $\alpha$ -olefin and ethylene and hydrogen in a ratio of 1 to 3 mol % to ethylene is polymerized. The polymer product from the first reactor has a high load melt index of 0,2 to 5 g/10 min and a density of 0,89 to 0,94 g/cm<sup>3</sup>. The product of the second reactor has a melt index of 80 to 1000 and a density of 0,920 to 0,970 g/cm<sup>3</sup>. The final blend has a density of preferably 0,920 to 0,955 g/cm<sup>3</sup> and a preferred molecular weight distribution of 20 to 30. The composition is used for high melt strength films having a high bubble stability and a high dart impact. The resin is extruded under a controlled level of oxygen.

**D2** relates to a multimodal polyethylene blend for blown films, prepared in a multistep process using Ziegler-type catalyst. The resin has a density of 940-970 kg/m<sup>3</sup> and is extruded in the presence of oxygen. It appears that the resin fulfills the requirements of the present claims.

Therefore, the subject-matter of the present application lacks novelty regarding D1 and D2.

## **2. Inventive step (Article 33(3) PCT)**

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of **claims 1 - 25** does not involve an inventive step in the sense of Article 33(3) PCT.

**D3** discloses a relatively high molecular weight, high density ethylene polymer blend for film forming. The blend has a density of preferably 0.90 - 0,960 g/cm<sup>3</sup>, a melt flow index (21) of at least 2 g/10 min and a polydispersity of at least 8. The blend consists of at least 30 wt % of a high molecular weight component having a density of preferably 0,930 to 0.9450 g/cm<sup>3</sup>, a melt flow index (21) of preferably 0.2 - 5 g/10 min. The low molecular

weight component has a density of preferably 0.950 to 0,978 g/cm<sup>3</sup> and a melt index (2) no greater than about 1000 g/10 min. According to these parameters it appears that the produced resin fulfills the requirements of the present product. The only distinguishing feature of the process is that the oxygen treatment is missing.

**D4** discloses the production of bimodal polymer blends for film forming by contacting in a first gas phase fluidized bed reaction zone a gaseous composition comprising a major proportion of ethylene and optionally hydrogen, with a Ziegler-Natta or coordination catalyst comprising a transition metal compound at a hydrogen/ethylene molar ratio below 0,3 to produce a high molecular weight polymer, transferring this product to a second gas phase fluidized bed reaction zone into which is also fed hydrogen and a gaseous monomeric composition at a hydrogen/ethylene rate of at least 0.9 and 8.0 times that in zone 1. It appears that the same polymers are produced as in the present claims. The resins of the examples was formed to a film having good bubble stability and a high dart drop resistance.

The only distinguishing feature of the process is that the oxygen treatment is missing.

**D5** discloses an ethylene polymer resin for film forming, prepared in a two step gas phase process using a titanium/magnesium Ziegler-Natta catalyst having a density of at least 0.940 -0,960 g/cm<sup>3</sup>. The resin consists of a high molecular weight part and a low molecular weight part. According to the parameters disclosed in paragraphs 0030, 0037 and 0038 it appears that the produced resin fulfills the requirements of the present product. The only distinguishing feature of the process is that the oxygen treatment is missing.

Taking D3, D4 or D4 as the closest prior art, the only difference to the subject-matter of the present application is, that the process described therein lacks the technical feature of oxygen treatment by extruding the resin to a film.

The technical effect resulting from this technical feature only appears to be an improved bubble stability and a high dart impact.

Therefore, it appears that the objective technical problem to be solved was, to provide a process for producing polyethylene resin based films having an improved bubble stability and a high dart impact.

**D6** relates to a process for producing polyethylene film composition having improved bubble stability. The composition is bimodal, has a molecular weight distribution of greater than 15, a density of 0,92 to 0,970 and comprises a high molecular weight and a low molecular weight part. The composition is extruded at a temperature of from 195 to 285 ° C. in the presence of oxygen in an amount of from about 0.5 to about 6% by volume to improve bubble stability.

**D7** relates to a process for modifying a polyethylene in an extruder. The polyethylene is brought into contact with oxygen or a gas mixture containing oxygen in the extruder at a preferred temperature of 230 to 250 °C. The polymer is particularly suitable for films with an increased bubble stability. Furthermore, it appears from the examples and the tables that the polymer composition is similar to the one, which is subject-matter of the present claims.

Furthermore, **D8** discloses a process for the preparation of a bimodal polyethylene blend comprising passing the blend through one or more active sieves. The final blend has a preferred density of 0,916 to 0,960, a molecular weight distribution from 8 to 44. The high molecular weight polymer has a MFI (21) of 0,01 - 30 g/10 min. The low molecular weight polymer has a MFI (2,16) of 5 to 3000 g/10 min. The blend is used for films.

Therefore, an inventive step can not be acknowledged to the subject-matter of the present claims in view of **D3, D4, D5 and D6, D7 and D8, besides the fact that it lacks novelty, as outlined under point 1 .**

### **3 Industrial applicability (Article 33(4) PCT)**

Since the improvement of the production of polyethylene based films is an important technical subject, industrial applicability can be acknowledged.

#### **Re Item VII**

#### **Certain defects in the international application**



1. Although **claims 5, 10, 16 and 21** have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought. The aforementioned claims therefore lack conciseness and as such do not meet the requirements of Article 6 PCT.

2. Subject-matter of independent **claims 15 and 20** are products which appear not to be characterized by all essential technical features of the present application.

Subject-matter of claim 15 is a fabricated film which is not related to the polyethylene composition and the process for preparing this polyethylene composition, which are subject-matter of the present application. The connection between present claim 15 and the subject-matter of the present application is given by present claim 16. Since claim 15 does not contain the essential technical features of the present application, it is not clear and concise and can not be allowed according to Article 6 PCT and the Guidelines (in force from March 25, 2004) Chapter 5.33.

The same argumentation applies on independent claim 20, which is only connected to the subject-matter of the present application by claim 21.

Therefore, claims 15 and 20 are not acceptable and have to be redrafted by incorporating the subject-matter of claims 16 and 21.

3. Applicants attention is drawn to the fact, that **claims 10, 11, 14 and 21** are product-by-process claims.

Novelty can only be acknowledged to a **product** (obtainable by a process), if the product as such fulfills the requirements of novelty (see PCT Preliminary Examination Guidelines (in force from March 25, 2004) Chapter 5.26 and 5.27.

If the products, which are subject-matter of claims 10, 11, 14 and 21 are novel as such, the process related part is redundant.

If the process is novel, it could never be excluded, that this process would also be suitable to produce any product, which is state of the art.

In view of these objections it would appear appropriate to file a product claim for the polymer composition, characterized by product related technical features, a process claim, characterized by process related technical features and a product claim for a film, comprising the claimed polymer composition.

**Re Item VIII**

**Certain observations on the international application**

1. The application does not meet the requirements of Article 6 PCT, because **claim 1** is not clear.

The meaning of "active screens" in claim 1, line 24 can not be understood.

2. The application does not meet the requirements of Article 6 PCT, because **claims 5, 9, 12 and 15** are not clear.

The parameter "bubble stability" is unclear because it appears to be an unusual parameter in the sense of PCT Preliminary Examination Guidelines (in force from March 25, 2004) Chapter 5.36.

It is pointed out that such a parameter can not render characterizing subject-matter, whereon novelty could be based (see PCT Preliminary Examination Guidelines (in force from March 25, 2004) Chapter 12.04).

3. The application does not meet the requirements of Article 6 PCT, because **claims 19, 20, 21** are not clear.

The parameter "having a NCLS" is unclear because it appears to be an unusual parameter in the sense of PCT Preliminary Examination Guidelines (in force from March 25, 2004) Chapter 5.36.

It is pointed out that such a parameter can not render characterizing subject-matter, whereon novelty could be based (see PCT Preliminary Examination Guidelines (in force from March 25, 2004) Chapter 12.04).

4. The application does not meet the requirements of Article 6 PCT, because **claim 8** is not clear.

If a tailored composition according to claims 5 - 7 is prepared the melt flow ratio of the

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

International application No.

PCT/US2004/013975

composition if it were not tailored can not be determined.  
Therefore, claim 8 has to be deleted.

5. The expression “about” renders the scope of the claims unclear and has to be deleted throughout the claims and the description (see PCT Preliminary Examination Guidelines (in force from March 25, 2004) Chapter 5.38.

## CLAIMS

1. A process for producing a multimodal ethylene polymer, which process comprises the following steps:

5 1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having;

10 i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally  
ii) a mole ratio of hydrogen to ethylene of from about 0.001:1 to about 0.3:1,

to produce a high molecular weight polymer (HMW); and

15 2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, with a gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene less than that in Step 1 and of from about 0:0005:1 to about 0.01:1; and  
ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1 to form a polymer blend product; and

20 3) melting the polymer blend product in an extruder having a mixer vent wherein;

i) the mixer vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and  
ii) the extrusion temperature is sufficient to melt the polymer and  
25 achieve tailoring in the presence of oxygen; and

4) passing the molten polymer blend through one or more active screens, wherein in the case of two or more active screens, the screens are positioned in series; each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 5 to about 100 lb/hr/in<sup>2</sup> (1.0 to 20 kg/s/m<sup>2</sup>) to  
30 form a screened molten polymer blend.

2. The process of Claim 1 wherein;

1) the gaseous composition in Step 1) has;

i) a mole ratio of alpha-olefin to ethylene of from about 0.02:1 to about 0.35:1; and

Empf.zeit:16/11/2004 16:43

Empf.nr.:741 P.003

- ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 0.2:1, and
- 2) the gaseous composition in Step 2) has;
- 5 i) a mole ratio of alpha-olefin to ethylene of less than or equal to about 0.007:1; and optionally
- ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.5:1 to about 2.2:1;
- 3) in Step 3, the extrusion temperature is from about 220 to about 270 °C; and wherein the ratio of the weight of polymer prepared in the first gas phase
- 10 reactor used in Step 1) to the weight of polymer prepared in the second gas phase reactor used in Step 2) is in the range of about 30:70 to about 70:30.
3. The process of Claim 2 wherein the ratio of the weight of polymer prepared in the first gas phase reactor used in Step 1 to the weight of polymer prepared in the second
- 15 gas phase reactor used in Step 2 is in the range of about 40:60 to about 60:40; the mole ratio of alpha olefin to ethylene in Step 1 is from about 0.02:1 to about 0.35:1 and in Step 2 is from about 0.001:1 to about 0.007:1; and in Step 3, the extrusion temperature is from about 230 to about 260 °C.
4. The process of any of Claims 1 through 3 wherein the polymer produced in Step 2 has a density of from 0.970 to 0.975 g/cm<sup>3</sup>.
- 20 5. A multimodal polyethylene composition having;
- 1) a density of at least about 0.940 g/cm<sup>3</sup> as measured by ASTM Method D-1505;
- 2) a melt flow index (I<sub>5</sub>) of from about 0.2 to about 1.5 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 5 kilograms);
- 25 3) a melt flow index ratio (I<sub>21</sub>/I<sub>5</sub>) of from about 20 to about 50;
- 4) a molecular weight distribution, Mw/Mn, of from about 20 to about 40; and
- 5) a bubble stability measured on an HS50S stationary extrusion system with an BF 10-25 die, HK 300 air ring, A8 take off, and WS8 surface winder, all
- 30 commercially available from Hosokawa Alpine Corporation, with a 100 mm die diameter having a 50 mm 21:1 L/D grooved feed extruder used according to the conditions described herein for a film of about 6 X 10<sup>-6</sup> m thickness of at least about 1.22 m/s line speed, at least about 45 kg/hr (0.013 kg/sec) output rate, or at least about 0.5 lb/hr/rpm (0.0000011 kg/s/rps) specific output rate or a combination thereof.

6) a dart impact on 12.5 micron ( $1.25 \times 10^{-5}$  m) film of at least 300 g;  
measured according to ASTM 1709, Method A;  
the composition comprising;

A) a high molecular weight fraction which;

- 5 a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);  
b) has a density of at least about  $0.860 \text{ g/cm}^3$  as measured by ASTM D-1505;  
c) has a melt flow index ( $I_{21}$ ) of from about 0.01 to about 50  
10 g/10 min (as measured by ASTM D-1238, measured at  $190^\circ\text{C}$  and 21.6 kilograms); and  
d) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 6 to about 12;  
and

B) a low molecular weight fraction which;

- 15 a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);  
b) has a density of at least about  $0.900 \text{ g/cm}^3$  as measured by ASTM D-1505;  
c) has a melt flow index ( $I_2$ ) of from about 0.5 to about 3000  
20 g/10 min (as measured by ASTM D-1238, measured at  $190^\circ\text{C}$  and 2.16 kilograms);  
d) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 5 to about 15;  
and  
e) is prepared using a mole ratio of alpha olefin to ethylene less  
25 than that in the high molecular weight fraction of less than or equal to about 0.01:1.

6. The multimodal polyethylene composition of Claim 5 wherein;

- 1) the density is from about  $0.945$  to about  $0.955 \text{ g/cm}^3$ ;  
2) the melt flow index ( $I_5$ ) is of from about 0.25 to about 1.0 g/10 min;  
30 3) the melt flow index ratio ( $I_{21}/I_5$ ) is of from about 24 to about 40;  
4) the molecular weight distribution,  $M_w/M_n$  is from about 22 to about 38;  
and

5) the bubble stability is greater than about 1.32 m/s line speed or from about 0.0000017 to 0.000027 kg/s/rps specific output rate or a combination thereof;

Empf.zeit: 16/11/2004 16:44

Empf.nr.: 741 P.005

the composition comprising;

A) a high molecular weight fraction which;

- a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);
- b) has a density of from about 0.890 to about 0.940 g/cm<sup>3</sup>;
- c) has a melt flow index (I<sub>21</sub>) of from about 0.2 to about 12 g/10 min; and
- d) a melt flow index ratio (I<sub>21</sub>/I<sub>5</sub>) of from about 7 to about 12; and

B) a low molecular weight fraction which;

- a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);
- b) has a density of from about 0.910 to about 0.975 g/cm<sup>3</sup>;
- c) has a melt flow index (I<sub>2</sub>) of from about 1.0 to about 1,000 g/10 min;
- d) a melt flow index ratio (I<sub>21</sub>/I<sub>5</sub>) of from about 6 to about 12; and
- e) the ratio of alpha olefin to ethylene is less than that in the high molecular weight fraction and less than or equal to about 0.01:1.

7. The multimodal polyethylene composition of Claim 6 wherein;

1) the molecular weight measured by Gel Permeation Chromatography is from about 90,000 to about 420,000.

2) the bubble stability is reflected in an output rate of from about 0.013 to 0.13

kg/s;

the composition comprising;

A) a high molecular weight fraction which;

a) has a melt flow index (I<sub>21</sub>) of from about 0.2 to about 0.4 g/10 min; and

b) a molecular weight of from about 135,000 to about 445,000;

c) is prepared using a mole ratio of alpha olefin to ethylene of from about 0.02:1 to about 0.35:1 and

B) a low molecular weight fraction which;

a) has a density of from about 0.970 to about 0.975 g/cm<sup>3</sup>;

Empf.zeit:16/11/2004 16:44

Empf.nr.:741 P.006

b) has a molecular weight of from about 15,800 to about 35,000; and

c) is prepared using a mole ratio of alpha olefin to ethylene of less than or equal to about 0.007:1.

5 8. The multimodal polyethylene composition of any of Claims 5 through 7 wherein the composition is tailored sufficiently to produce an increase of melt flow ratio ( $I_{21}/I_5$ ) of from about 1 to about 4 units as compared with the same composition without tailoring.

9. The multimodal polyethylene composition of any of Claims 5 through 7 which;

- 10 i) when fabricated into a film of 0.5 mils ( $1.27 \times 10^{-5}$  m) thickness, has a dart impact of greater than about 400 g;
- ii) when fabricated into a film of 1.0 mils ( $2.54 \times 10^{-5}$  m) thickness, has a film appearance rating of greater than or equal to 20; and
- 15 iii) when fabricated into a blown film has (a) a bubble stability of at least about 240 ft/min (1.22 m/s) line speed, (b) can be used to produce blown film of 6 micron ( $6 \times 10^{-6}$  m) thickness at actual output rates of from about 50 to about 1100 lb/hr (0.0063 to 0.14 kg/s) or (c) specific output rates of from about 0.5 to about 15 lb/hr/rpm ( $1.05 \times 10^{-6}$  to  $3.15 \times 10^{-5}$  kg/s/rps), or a combination of at least 2 of (a), (b) and (c).

20 10. The multimodal polyethylene composition of Claim 5 produced by a process comprising:

1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having;

- 25 i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally
- ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.001:1 to about 0.3:1,

30 to produce a high molecular weight polymer (HMW); and

2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, with a gaseous composition having;



i) a mole ratio of alpha-olefin to ethylene of from about 0:0005:1 to about 0.01:1; and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1

to form a polymer blend product; and

3) melting the polymer blend product in an extruder having a mixer vent wherein;

i) the mixer vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and

ii) the extrusion temperature is sufficient to melt the polymer and result in tailoring in the presence of the oxygen; and

4) passing the molten polymer blend through one or more active screens, wherein in the case of two or more active screens, the screens are positioned in series, each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 5 to about 100 lb/hr/in<sup>2</sup> (1.0 to 20 kg/s/m<sup>2</sup>) to form a screened molten polymer blend.

11. The multimodal polyethylene composition of Claim 10 wherein in the process;

1) the gaseous composition in step 1) has;

i) a mole ratio of alpha-olefin to ethylene of from about 0.02:1 to about 0.35:1; and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 0.2:1, and

2) the gaseous composition in step 2) has;

i) a mole ratio of alpha-olefin to ethylene of from about 0.001:1 to about 0.007:1; and optionally

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.5:1 to about 2.2:1; and

wherein

3) the ratio of the weight of polymer prepared in the first gas phase reactor used in step 1) to the weight of polymer prepared in the second gas phase reactor used in step 2) is in the range of about 30:70 to about 70:30.

12. The multimodal polyethylene composition of Claim 10 or 11 which, when fabricated into a film using a HS50S stationary extrusion system with an BF

10-25 die, HK 300 air ring, A8 take off, and WS8 surface winder, all commercially available from Hosokawa Alpine Corporation, with a 100 mm die diameter having a 50 mm 21:1 L/D grooved feed extruder has a vertical bubble stability described by:

5 Alpine film line vertical bubble stability (in ft/min) =  $275.05 - 0.000081 * Mz + 0.0000735 * Mz+1 (BB) + 0.0001312 * \text{viscosity (P)} @ 0.1 \text{ sec}^{-1} \text{ shear rate} + 1.0033E-9 * (\text{viscosity (P)} @ 0.1 \text{ sec}^{-1} \text{ shear rate})^2 - 0.026764 * \text{viscosity (P)} @ 100 \text{ sec}^{-1} \text{ shear rate}$  [where (BB) is backbone, E is exponent of base 10] or

10 Alpine film line vertical bubble stability (in m/s) =  $\{0.005\} \{275.05 - 0.000081 * Mz + 0.0000735 * Mz+1 (BB) + (0.0001312 * 0.1 * \text{viscosity (Pa}\cdot\text{s)} @ 0.1 \text{ sec}^{-1} \text{ shear rate}) + 1.0033E-9 * [(0.1) (\text{viscosity (Pa}\cdot\text{s)} @ 0.1 \text{ sec}^{-1} \text{ shear rate})]^2 - (0.026764 * 0.1 * \text{viscosity (Pa}\cdot\text{s)} @ 100 \text{ sec}^{-1} \text{ shear rate})\}$

13. The multimodal polyethylene composition of Claim 10 or 11 wherein when  
15 made into a film has a Dart Drop calculatable using the equation: Dart drop (g) =  $469.9 - 54.8 * (G'/G'' @ 0.01 \text{ shear rate}) - 91.4 (G'/G'' @ 0.01 \text{ shear rate})^2$ .

14. A film comprising the multimodal polyethylene composition of Claim 10 or 11.

15. A multimodal modal polyethylene film which;

- 20 i) when fabricated into a film of 0.5 mils ( $1.27 \times 10^{-5} \text{ m}$ ) thickness has a dart impact strength of greater than about 300 g,
- ii) when fabricated into a film of 1.0 mils ( $2.54 \times 10^{-5} \text{ m}$ ) thickness has a film appearance rating of greater than or equal to 20; and
- 25 iii) when fabricated into a film of 6 microns (micrometers) ( $6 \times 10^{-6} \text{ m}$ ) has a bubble stability of at least about 260 ft/min (1.32 m/s) line speed.

16. The film of Claim 15 wherein the dart impact strength is greater than about 400 g, the film appearance rating is greater than or equal to 30 and the bubble stability is at least about 250 ft/min (1.27 m/s), the film comprising a multimodal polyethylene  
30 composition having;

- 1) a density of at least about  $0.940 \text{ g/cm}^3$  as measured by ASTM D-1505;
- 2) a melt flow index ( $I_5$ ) of from about 0.2 to about 1.5 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 5 kilograms);
- 3) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 20 to about 50; and

4) a molecular weight distribution,  $M_w/M_n$ , of from about 20 to about 40;  
the composition comprising;

A) a high molecular weight fraction which;

- a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);
- b) has a density of at least about  $0.860 \text{ g/cm}^3$  as measured by ASTM D-1505;
- c) has a melt flow index ( $I_{21}$ ) of from about 0.01 to about 50 g/10 min (as measured by ASTM D-1238, measured at  $190^\circ\text{C}$  and 21.6 kilograms); and
- d) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 6 to about 15; and

B) a low molecular weight fraction which;

- a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition);
- b) has a density of at least about  $0.900 \text{ g/cm}^3$  as measured by ASTM D-1505;
- c) has a melt flow index ( $I_2$ ) of from about 0.5 to about 3000 g/10 min (as measured by ASTM D-1238, measured at  $190^\circ\text{C}$  and 2.16 kilograms); and
- d) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 5 to about 15.

17. The film of Claim 16 wherein the dart impact strength is greater than about 420 g, the film appearance rating of greater than or equal to 30 and the bubble stability is at least about 250 ft/min (1.27 m/s), and wherein for the multimodal polyethylene composition;

- 1) the density is from about  $0.945$  to about  $0.955 \text{ g/cm}^3$ ;
- 2) the melt flow index ( $I_5$ ) is of from about 0.25 to about 1.0 g/10 min;
- 3) the melt flow index ratio ( $I_{21}/I_5$ ) is of from about 24 to about 40; and
- 4) the molecular weight distribution,  $M_w/M_n$  is from about 22 to about 38;

the composition comprising;

A) a high molecular weight fraction which;

- a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);
- b) has a density of from about  $0.890$  to about  $0.940 \text{ g/cm}^3$ ;

c) has a melt flow index ( $I_{21}$ ) of from about 0.2 to about 12 g/10 min; and

d) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 7 to about 12; and

5

B) a low molecular weight fraction which;

a) is present in an amount of from about 40 to about 60 weight percent (based on the total weight of the composition);

b) has a density of from about 0.910 to about 0.975 g/cm<sup>3</sup>;

10

c) has a melt flow index ( $I_2$ ) of from about 1.0 to about 1,000 g/10 min; and

d) a melt flow index ratio ( $I_{21}/I_5$ ) of from about 6 to about 12.

18. The film of Claim 17 having a dart impact strength of greater than about 400 g, a film appearance rating of greater than or equal to 40, and a bubble stability of at least about 260 ft/min (1.32 m/s).

15

19. The multimodal polyethylene composition of any of Claims 5, 6, 7, 10 or 11 having a NCLS of at least 2400 hours, a ratio of flexural modulus to density of at least 1140 kPa • m<sup>3</sup>/kg or both.

20. A multimodal polyethylene composition having a NCLS of at least 2400 hours, a ratio of flexural modulus to density of at least 1140 kPa • m<sup>3</sup>/kg, and an  $I_{21}/I_2$  of at

20

least 90.

21. A multimodal polyethylene composition having a NCLS of at least 2400 hours, and a ratio of flexural modulus to density of at least  $1140 \text{ kPa} \cdot \text{m}^3/\text{kg}$  produced by a process comprising:

1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about  $70^\circ\text{C}$  to about  $110^\circ\text{C}$ , a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.001:1 to about 0.3:1,

to produce a high molecular weight polymer (HMW); and

2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about  $70^\circ\text{C}$  to about  $110^\circ\text{C}$ , with a gaseous composition having;

i) a mole ratio of alpha-olefin to ethylene of from about 0.0005:1 to about 0.01:1; and

ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1

to form a polymer blend product; and

3) melting the polymer blend product in an extruder having a mixer vent wherein;

i) the mixer vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and

ii) the extrusion temperature is sufficient to melt the polymer and result in tailoring in the presence of the oxygen; and

4) passing the molten polymer blend through one or more active screens, wherein in the case of two or more active screens, the screens are positioned in series, each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 5 to about  $100 \text{ lb/hr/in}^2$  ( $1.0$  to  $20 \text{ kg/s/m}^2$ ) to form a screened molten polymer blend.

22. A fabricated article made of the multimodal polyethylene composition of any of Claims 19, 20 or 21.

23. The fabricated article of Claim 22 which is a fiber, a wire or cable jacket, a conduit, a tape, a sheet, a pipe, a blow molded object, an injection molded object, a vacuum molded object, a rotomolded object, a thermoformed object or a combination thereof.

5 24. The fabricated article of Claim 23 which is a single layer or multilayer corrugated pipe.

25. The fabricated article of Claim 22 which is a multilayer structure having at least one layer having corrugation or other strength enhancing shape and at least one smooth layer.

10

Empf.zeit: 16/11/2004 16:46

Empf.nr.: 741 P.013